OTS: 60-31206

JPRS: 3339

26 May 1960

THE APPLICATION OF POWERFUL SOURCES OF RADIATION IN INDUSTRY

- USSR -

by G. I. Grafov and V. I. Sinitsyn

Distributed by:

OFFICE OF TECHNICAL SERVICES
DEPARTMENT OF COMMERCE
WASHINGTON 25, D. C.

U. S. JOINT PUBLICATIONS RESEARCH SERVICE
205 EAST 42nd STREET, SUITE 300
NEW YORK 17, N. Y.

F O R E W O R D

This publication was prepared under contract by the UNITED STATES JOINT PUBLICATIONS RESEARCH SERVICE, a federal government organization established to service the translation and research needs of the various government departments.

JPRS: 3339
CSO: 3625-D

THE APPLICATION OF POWERFUL SOURCES OF RADIATION IN INDUSTRY

- USSR -

[Following is a translation of an article by G. I. Grafov and V. I. Sinitsyn in Inzhenro-fizicheskiy zhurnal (Physico-engineering Journal), Vol. III, No. 2, Minsk, February 1960, pages 128-132.]

A conference on the application of powerful sources of radiation in industry, particularly in the chemical industry, organized by the International Agency on Atomic Energy and the first large international conference devoted wholly to the role of ionizing radiation in industrial processes, was held in Warsaw in the period 8-12 September 1959.

Read and discussed at the conference were more than 60 papers touching upon concrete problems of the use of radiation in industry, and also certain allied scientific, technological, and economic problems. A brief survey is given below of the materials presented at the conference.

THE ACTION OF RADIATION ON PLASTICS AND ELASTOMERS

With his paper "The Physical Properties of United Polyvinyl Chloride Chains of Copolymers Obtained as a Result of the Action of Ionizing Radiation" the English scientist S. K. Pinner showed that it is possible to obtain products with strong cross-linking with relatively small doses of ionizing radiation by adding diallyl and triallyl ethers to polyvinyl chloride prior to irradiation. Tests of the physical properties of these products indicate that they are not simple graphite copolymers, which are ordinarily connected with the presence of long branched chains, but united allyl polymer bonds.

Several papers were presented by Japanese scientists. In order to study radiation chemical processes in several polymers, Shunichi Onisi and others measured the spectra of the electronic spin resonance of γ-irradiated polymers. Spectra of electronic spin resonance can be complex and broad for a number of reasons; thus recognition of included radicals turned out to be difficult in many cases. In the cases of certain irradiated polymers, such as nylon, polyethylene, and polyvinyl alcohol, the spectra of built-up, nonbuilt-up, and heat-treated samples differed from one another. On the other hand, builing up, doubling the orientation, and heat treating did not create different spectra in the case of tetrone (polyethylene phthalate).

M. Matsumoto and A. Danno (Japan) studied the action of radiation on polyvinyl alcohol. They found that the process of shortening the molecular chains took place in the region of low dosages of radiation on the order of 10^7 r (emitter, Co^{60}), independent of the dose rate of radiation. When large doses of radiation were used, the greater the dose rate, the greater the ease with which the polyvinyl alcohol acquired cross-linkages. Irradiation in vacuo caused gelation at low dosage rates and with smaller total doses than was the case with irradiation in air. These studies indicated the marked influence of oxygen in the radiation process which could be found either in aqueous solutions or which could penetrate into a solid body from the surface of the sample.

Duh. Oster studied the chemical action of ultraviolet rays on the same polymers which have been studied up to this time under the action of ionizing radiation. It turned out that in the case of polyethylene and many other high polymers, irradiation with ultraviolet rays caused crosslinking. Thus many chemical results from photochemical reactions are similar to the results of ionizing radiation.

THE EFFECT OF RADIATION ON THE PROCESSES OF POLYMERIZATION AND BUILDING-UP OF MACROMOLECULES, AND ITS EFFECT ON CHEMICAL REACTIONS

It was shown in the paper of S. S. Medvedev and others that the polymerization reaction of ethylene in solutions of heptane, cyclohexane, methyl alcohol, and acetone at a pressure of 5 atm, a temperature of 25° C, and a dose rate of 98 r/sec proceeds at a rate of 10-15 times faster than in the gas phase. The polymers that form have an average molecular weight of 20,000-40,000. The rate of the polymerization process in the gas phase increases with time in the initial stages, then becomes constant. A decrease in the polymerization rate is observed in the late stages. The radiation-chemical output at a pressure of 300 atm, temperature of 25° C, and a dose rate of 72 r/sec/ amounts to 4,300-6,500 molecules of ethylene per 100 ev of absorbed energy.

Ye. V. Barelko and others demonstrated with a number of examples the role of radiation as an initiator whose action is, in many cases, expediently stopped at the beginning of the reaction, thus ensuring the smallest consumption of radiation energy per unit of reaction product. The principle of sensitizing the radiation initiation of transformations of radiation-resistant substances with chemically inert but radiation-unstable substances was formulated and based on the example of the process of the oxidation of benzol, which has been studied in detail.

The English scientists F. Dalton and R. Roberts (Wantage Radiation Laboratory) studied the effect of γ-radiation from cobalt-60 on a solution of acrylonitrite in poly-dimethylsiloxane. The degree of polymerization of the acrylonitrite was determined by a dilatometric method. The relationship of the speed of the polymerization reaction to the monomer concentration, the intensity of radiation, and the temperature was determined and given a kinetic explanation.

S. Okamura and others (Japan) studied the processes of the polymerization building-up of surface and internal layers of nylon fibers under the action of γ-radiation from Co^{60}. It was discovered that when nylon fibers in a nitrogen atmosphere were irradiated, a gel was formed while shortening of the molecular chains took place in air. After the fibers were irradiated in nitrogen, they were immersed in an aqueous solution of acrylamide, then irradiated again. Under such processing, polymerization building-up took place exclusively on the surface of the fiber. In air, building-up also took place in the internal layers of the fibers, as shown by photographic studies. The authors achieved an increase in size of several hundred percent over the initial weight of the fibers, at the same time maintaining their tensile strength by processing the fibers in a 5% solution of methanol formamide and subsequent irradiation of the fibers with Co^{60} in a methanol solution of styrene.

In order to improve the properties of motion-picture film and fibers of polyvinyl, research was done in the Kyoto and Osaka laboratories of the Japanese Association for the Radiation Study of Polymers (I. Sakurada and others) on the graphite copolymerization of different vinyl monomers with motion-picture films made of polyvinyl by using γ-irradiation. It was found that the action of methyl methacrilate in grafting films made of polyvinyl was analogous to the action of styrene. The presence of water in the monomer solution aided grafting. The maximum value for grafting reached 4,000% and was obtained with a dosage of γ-radiation equal to 5×10^5 r.

Dzh. V. Suterland and A. O. Allen (USA, Brookhaven National Laboratory) studied the radiolysis of pentane included in the crystalline lattice of dehydrated synthetic zeolites. For a sodium zeolite, the hydrogen yield changes little, depending upon the amount of pentane in the zeolite. Partial replacement of sodium ions by manganese ions reduced the hydrogen yield, but replacement by cobalt ions caused the hydrogen yield to be increased many times.

The French scientists M. Dyuryu and others studied the formation of peroxides of certain hydrocarbons (cumene, isooctane, and others) under γ-irradiation. This research showed that chain reactions of oxidation of the hydrocarbons under radiation can occur independently of the temperature and, at the same time, the rate of formation of peroxides becomes quite high while the secondary reactions, for example the decomposition of the peroxide that is forming, remain insignificant.

F. Trenar and P. Verrye (French Petroleum Institute) studied processes of chlorination of a carbon chain containing the COO group. Under irradiation, the chlorine dissolved to the point of saturation in one of its liquid derivatives replaced one atom of hydrogen in the carbon chain. This reaction has the character of a chain process. Radicals are formed under radiolytic decomposition of the liquid medium while the chlorine is the agent of chain formation. The G value is very high and can exceed 10^5, thus the chlorinating reaction is economically profitable and one can foresee its industrial application. Monochlorinated and dichlorinated propionic acids and ethers lead to corresponding acrylic derivatives. Chlorination can be carried out to the extreme stage of substituting five atoms of hydrogen in the carbon chain and even up to the point of obtaining the chloride of pentachloro propionic acid, thus producing a whole series of wholly reproducible and frequently crystallizing products.

By using strong beams of high-energy electrons, A. Khengleyn (USA) synthesized new dechloro phosphine preparations and preparations of nitroso compounds. The dichloro phosphines can be synthesized directly from phosphorus dichloride and aliphatic or aromatic hydrocarbons. The new nitroso compounds can be synthesized by introducing free radicals into nitric oxide. The trichloride of nitroso-methane is formed in a CCl_4--NO mixture, while the dichloride of nitroso-methane, which had not been synthesized previously, is formed in a mixture of $CHCl_3$--NO. The polymer was probably obtained in the PCl_3--NO mixture by polymerization of the intermediate nitroso-phosphine dichloride.

A. S. Kuz'minskiy and others (USSR) used ionizing radiation to vulcanize silicone rubber. Radiation vulcanization of this rubber did not require the use of peroxide vulcanizers (their presence had a negative effect on the exploitation of such rubbers), high temperatures, or subsequent curing in a thermostat. Radiation vulcanization of polydimethyl siloxane requires smaller integral doses and consequently can be carried out in a shorter time than for many other types of rubber. Radiation-vulcanized products of silicone rubber possess a number of advantages over peroxide vulcanization products (thermal aging, chemical relaxation of stresses, accumulation of residual deformation under compression).

It was shown in the paper by A. V. Topchiyev, L.S . Polak, and others (USSR) "The Prospects for Industrial Use of Radiation-Thermal Cracking of Normal Hydrocarbons" that as the temperature was raised, the composition of the products of radiation-thermal cracking (RTC) shifted more and more toward the composition of ordinary thermal cracking even though the RTC took place at temperatures not employed in ordinary thermal cracking. Thus, by raising the temperature of radiolysis of hydrocarbons, it is possible to increase the radiation yields of product to practically acceptable levels. At the same time, the yields of the products of most interest to industry, the unsaturated compounds, show the greatest increases.

POWERFUL SOURCES OF RADIATION AND METHODS FOR USING THEM IN INDUSTRY

The paper presented by A. Danno contained a description of the design of a 10-kilocurie cobalt-60 source for studying the effects of irradiation on organic compounds, polymers, and nonmetallic materials. In order to provide even distribution of the dosage while irradiating comparatively large samples, a cylindrical radiating device was designed which was made of 110 cobalt rods, each with a diameter of 3 mm and a length of 125 mm. The specific activity per rod amounted to about 10 kilocuries per gram. Two rods were inserted in a stainless steel pipe with a wall thickness of 0.3 mm. These pipes were assembled concentrically in two cylindrical shells with diameters of 10 and 11.8 cm. The dimensions of the cylindrical source were as follows: height 40.5 cm, external diameter 13.4 cm, and internal diameter 8.6 cm. The source could be separated into two cylinders: the interior consisting of 30 pipes placed equidistant from each other, and the exterior consisting of 25 pipes. Thus it was possible to obtain a field of three different dose rates, depending upon whether the interior and exterior cylinders were used simultaneously or separately.

D. U. Georg and D.N. Gregori presented a description of the γ-apparatus of the Research Center of the Australian Commission for Atomic Energy in which the TVEL of the HIFAR experimental reactor was used. After being removed from the reactor, the fuel elements were kept in a water-cooled storage chamber. The average activity of each TVEL was about 105 kilocalories. They were stored in 48 nests located in a square lattic with a lattice pitch of 178 mm. For irradiation, a vessel with a diameter of 228.6 mm was placed in the center of eight symmetrically-arranged nests for positioning the TVEL. The space available for irradiation had a diameter of about 178 mm and a length of 762 mm. The material to be irradiated was fastened to a protective plug and introduced or withdrawn from the irradiation pipe with the special vertical loading device for servicing the reactor. A system was provided for cooling the irradiated material, measuring its temperature, controlling the air in the chamber, and removing liquid or gaseous reaction products. The paper gave a description of a device for irradiating materials directly in the reactor.

The Soviet scientists N. P. Syrkus, A. Kh. Brecher, and B. I. Vaynshteyn stated the basic technological characteristics of apparatus for carrying out radiation chemical processes on an industrial scale. They suggested a method for evaluating the effectiveness of an apparatus of any design by comparing it with the productivity of an infinitely large apparatus with the very same radiation source. The authors calculated the technological characteristics of an apparatus for the radiation polymerization of ethylene (at a pressure of 200 atm and temperature of 25° C) with a cobalt-60 rod source for γ-radiation at different activities.

Problems connected with the application of radiation for irradiating food products, plants, and organism; problems of the economics of processing with radiation; and other items were also discussed at the conference.

5809

- END -